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Determining thermochemical properties of halogenated metals: On enabling the rapid assessment of agent defeat formulations

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Determining thermochemical properties of halogenated metals: On enabling the rapid assessment of agent defeat formulations

- UNCLASSIFIED –

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H. B. Radousky, Lawrence Livermore National Laboratory

* Significant year-four team effort/involvement

Basic Research Technical Review
July, 2015

Determining thermochemical properties of halogenated metals: On enabling the rapid assessment of agent defeat formulations
PIs: Joseph M. Zaug and Sorin Bastea - Lawrence Livermore National Laboratory
**BRCALL08-Per5-H-1-0052 (HDTRA-11-1-4538I)**

Objective: Yr.-4 To determine the equations of state (EoS) of predicted biocidal agent products using x-ray diffraction (solid state: $MgCl_2$, TiF_4, HI_3O_8) and laser based shockwave and acoustic techniques (fluid state: $(C_2H_5)_3PO_4$ (TEP), BiI_3). To provide semi-empirical Cheetah Code guidance to large-scale field tests

Method: Synchrotron-based X-ray diffraction, ultrafast tabletop shockwave and time domain interferometery, photoacoustic light scattering based acoustics and semi-empirical thermochemical code developments (Cheetah V.7)

Status of effort: MgCl2 –EoS determined to 30+ GPa –Cheetah code parameterization completed; $(C_2H_5)_3PO_4$ shock Hugoniot measured and an EOS has been developed and implemented in Cheetah; BiI_3 EOS has been developed and implemented in Cheetah; TiF_4 XRD based EOS study in progress, Laser Repair completed March 2015

Personnel Supported:
Elissaios Stavrou (PD) began work, Sept. 2014
LLNL staff scientists: J. Zaug, S. Bastea, Mike Armstrong, Jonathan Crowhurst, and H. Radousky
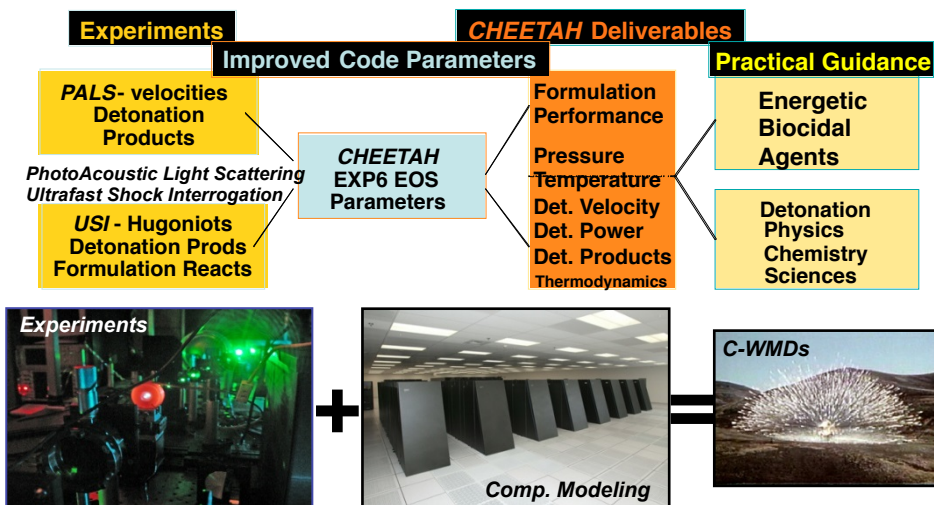
_Yr. # 1_: AlF_3, AlI_3, Ag_2O EOS development
_Yr. # 2_: MgF_2, BF_3, and I_2, EOS development; CHEETAH optimization tool development
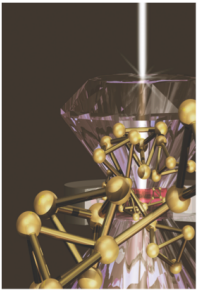_Yr. # 3_: $MgCl_2$, BiI_3 EOS begun, continued CHEETAH optimization tool development
_Yr. # 4_: $MgCl_2$, BiI_3, TEP, HI_3O_8, completed, TiF_4 dev.

Funding: Year 1: FY12-$224k, Year 2: FY13-$228k, Year 3: FY14-$228k; Year 4: FY15-$219K
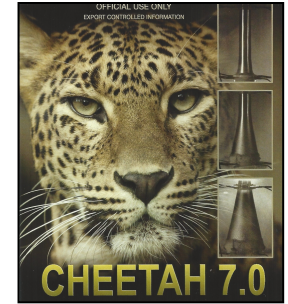
PI contact Information:
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Program Objective

- Semi-empirically determine shock chemistry equilibrium states e.g., P, T, V, [product conc.] of halogen loaded explosive formulations
  - DTRA C-WMD mission success requires basic thermochemical knowledge of shock chemistry states – required to optimize energetic release of engineered biocides with minimal unintended dispersal
  - We elucidate extreme P-T condition halogen chemistry
  - Pursuit of our objective benefits energy sciences including efforts to enhance the efficiency of propulsion drive power plants

Background and Significance

- Halogen, interhalogen, and halogen oxide gases oxidize and disrupt the action of bacterial cells -membrane function- related genes are repressed

- In aqueous environments, halogens produce hypohalous acids, which if produced in high enough concentrations can stress a bacterium into activating virulence factor genes leading to secretions of endo- or exotoxins.

- Silver and Iodine containing compounds are well-known biocidal agents

- Less selective agents could facilitate the antimicrobial action of a secondary agent nanoparticles (Amplify Toxicity*)

* J. Kim, B. Pitts, P. S. Stewart, A. Camper, and J. Yoon, "Comparison of the antimicrobial effects of chlorine, silver ion, and tobramycin on biofilm", Antimicrobial Agents and Chemotherapy **52** 1446, (2008).
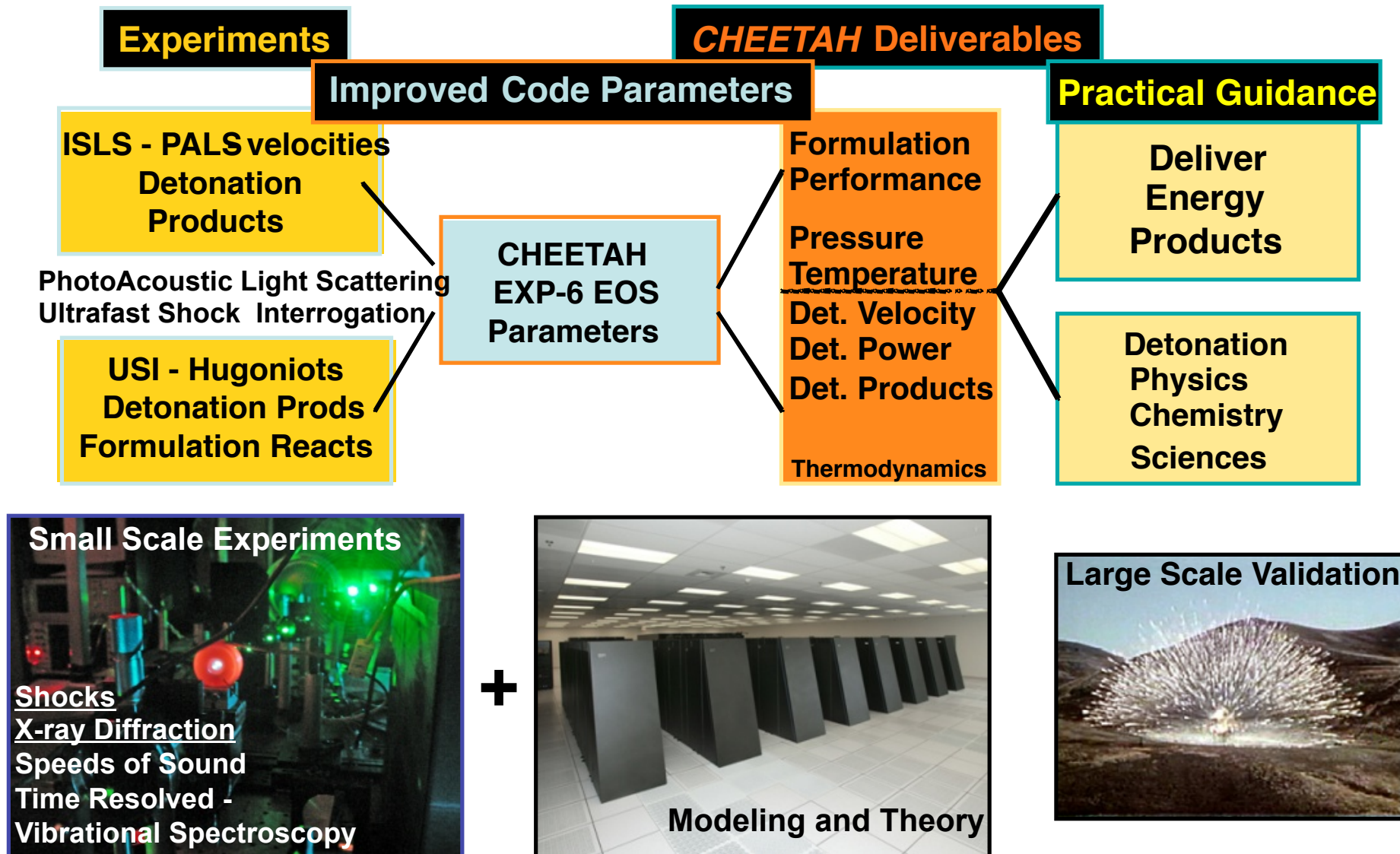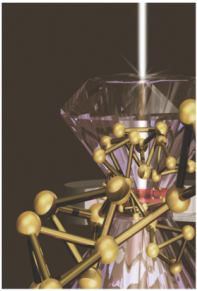
Background and Significance
Preliminary Work

Our team developed and tested unique experimental and computational infrastructures (DOE and DOD developments)

• Backreflected and Photoacoustic Light Scattering (BR/PALS) - sound speed, EoS characterization of fluids and mixtures (10's GPa, <1200 K)

• Ultrafast Shock Time Domain Interferometry (UTDI) – 1 ns shockless or shock state characterizations

• CHEETAH-code v.7 – EoS and interatomic potential library to predict detonation chemistry, (Typically <2% error in Detonation Performance Parameters)

> 550 interagency U.S. government users

Technical Approach

CHEETAH Deliverables

Improved Code Parameters

Practical Guidance

ISLS - PALS velocities Detonation Products

PhotoAcoustic Light Scattering
Ultrafast Shock Interrogation

USI - Hugoniots Detonation Prods Formulation Reacts

CHEETAH EXP-6 EOS Parameters

Formulation Performance

Pressure Temperature
Det. Velocity
Det. Power
Det. Products

Thermodynamics

Deliver Energy Products

Detonation Physics Chemistry Sciences

Small Scale Experiments

<u>Shocks</u>
<u>X-ray Diffraction</u>
Speeds of Sound
Time Resolved -
Vibrational Spectroscopy

+

Modeling and Theory

Large Scale Validation

Technical Approach - 1

Synchrotron X-ray Powder Diffraction - XRPD

- ## Static compression equations of state (EoS)

  > Stringently developed EOS libraries - interatomic interaction potentials to predict detonation chemistry

- ## V(P,T) EOS Data (T < 4-5 kK)

  XRPD is a well-accepted approach toward determining EOSs; materials structural information of general scientific importance; new molecules can be made - characterized

  > EOSs are determined rapidly, 2-3 days* e.g., surrogate agents, detonation products, polymers, HEs

* **After a sample is prepared**

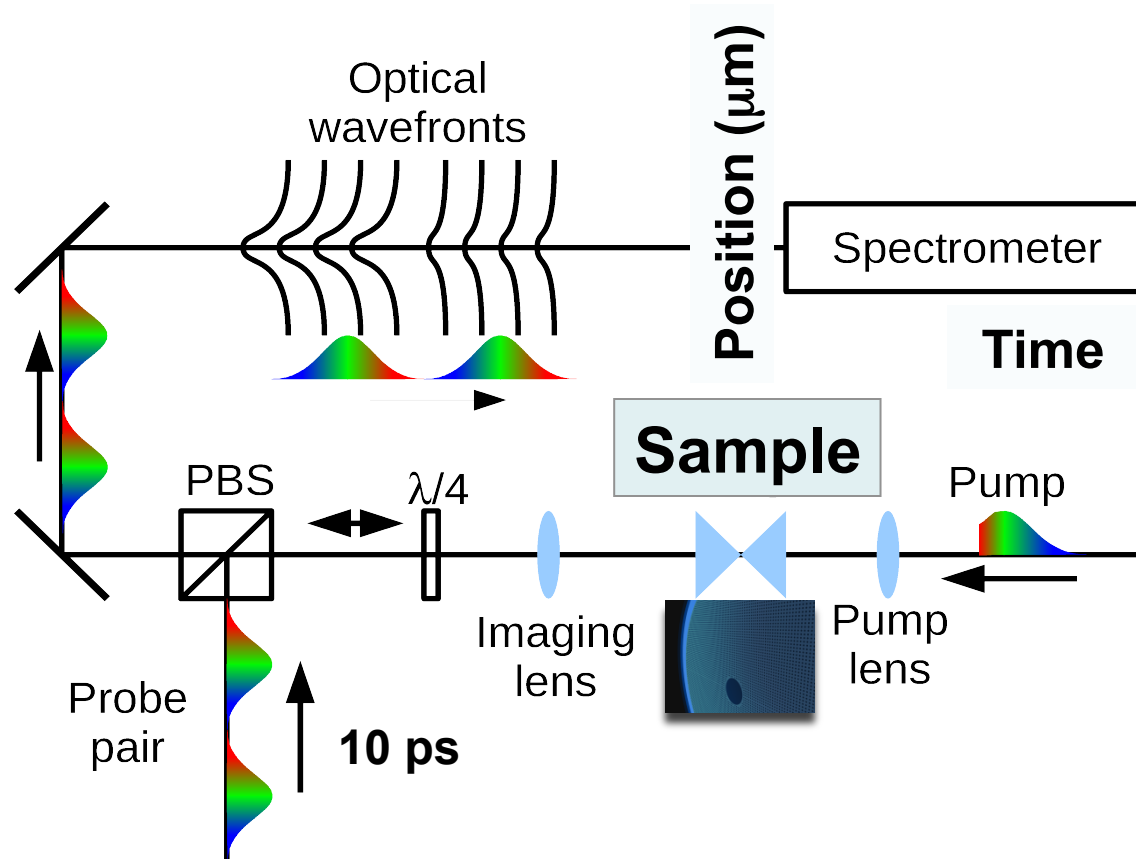# Technical Approach - 2

Ultrafast Time Domain Interferometry – UTDI

- ## Shock Hugoniot equations of state (EoS)

  > Stringently developed EOS libraries - interatomic interaction potentials to predict detonation chemistry

- ## Versatile – High Data Throughput

  UTDI is a tabletop ultrafast dynamic compression instrument - measures hydrodynamic properties of fluid- and solid-state materials – Compliments gas gun studies

  > EOSs (once a sample is ready) are determined rapidly, 2-3 days e.g., surrogate agents, detonation products, polymers, HEs

Ultrafast Time Domain Interferometry (UTDI) is a Method to Characterize Dynamic Response Phenomena

Optical wavefronts

Position (μm)

Spectrometer

Time

Sample

PBS

$\lambda/4$

Imaging lens

Pump lens

Pump

Probe pair

10 ps

Ultrafast TDI

Version 2.0

Footprint 60' square

Compression wave e.g., ramp, shock, generation and probe technique

> Mbar shock stress in free-standing Al (<3 μm thick)

Time res.   > 1 ps
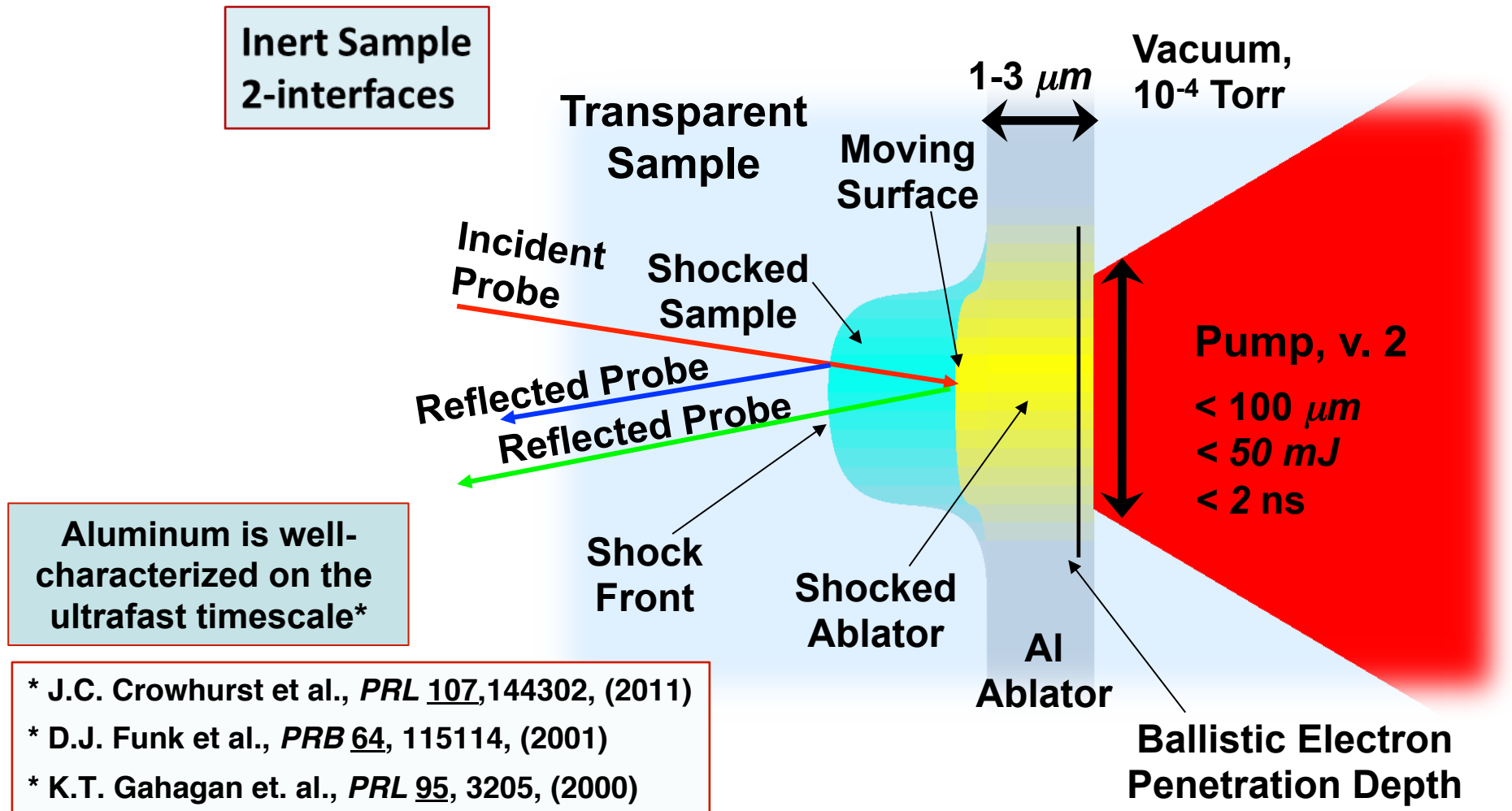
Spatial res. > 2 μm

Drive duration up to 1 ns

UTDI + analysis examples: M.R. Armstrong et al. *JAP* <u>108</u>, 023511, (2010)
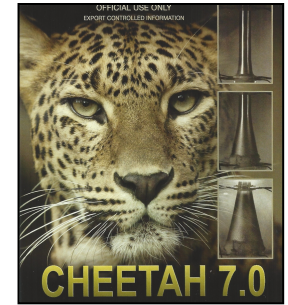
M.R. Armstrong et al. *APL* <u>92</u>, 101930, (2008)

UTDI is based on many other works

Tabletop Laser Based Shock Generation: A Small-Scale Experiment to Characterize Dynamic Properties

Inert Sample
2-interfaces

Transparent Sample

Moving Surface

1-3 μm

Vacuum, 10^{-4} Torr

Incident Probe

Shocked Sample

Reflected Probe

Reflected Probe

Pump, v. 2

< 100 μm
< 50 mJ
< 2 ns

Shock Front

Shocked Ablator

Al Ablator

Ballistic Electron Penetration Depth

Aluminum is well-characterized on the ultrafast timescale*

* J.C. Crowhurst et al., *PRL* 107,144302, (2011)
* D.J. Funk et al., *PRB* 64, 115114, (2001)
* K.T. Gahagan et. al., *PRL* 95, 3205, (2000)

To enhance clarity, this drawing is not-to-scale

Technical Approach - 3

Cheetah-Code

- The Scientific Cheetah engine consists of highly predictive EoS of fluids and solids at high P-T, which are employed in the context of detonation theory to calculate the performance of energetic materials.

- Well-tested theories for multi-component-multi-phase systems underlie the physics and chemistry components of Cheetah, rather than empirical approaches such as Jones-Wilkins-Lee (JWL EoS)

- Cheetah is currently the most reliable non-experimental method for testing and surveying explosives related concepts –is routinely used by DOD and DOE customers to optimize material formulations

- Well-over $ 1 B (2006 dollars) rigorously filtered (trusted) and incorporated experimental datasets

Cheetah is a highly predictive code

Cheetah performance for standard CHNO explosives (HMX, RDX, PETN, TNT, BTF, HNS, HNB, etc.)
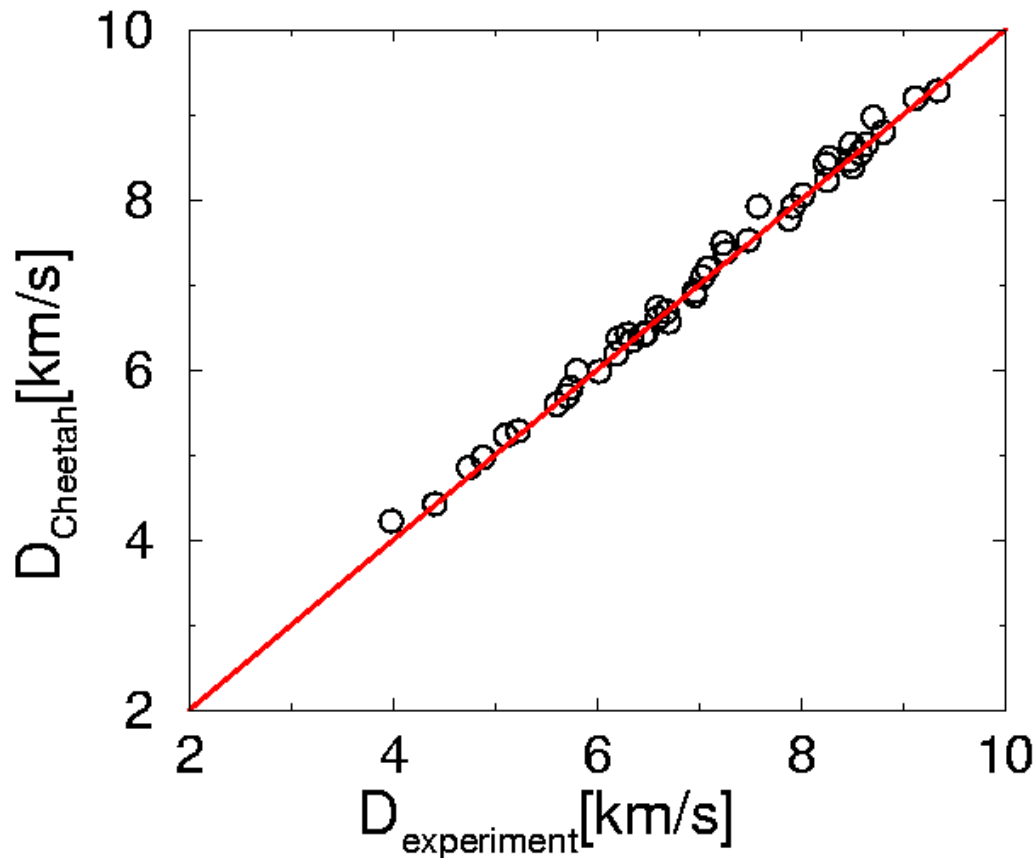
Cheetah broad areas for improvement

- Halogenated (F and Cl) compounds - ionic dissociation needs to be explicitly modeled
- Metal-loaded (e.g. Al, B, Si, W, Ti, P, etc.) formulations - new products (e.g. HBO_2, B_2O_3, SiO_2, BCl_3), equations of state for solids/liquids (e.g. B_2O_3, BN), melting lines etc., need to be modeled
- Very high nitrogen compounds – formation of CN type polymers and/or solids likely needs to be accounted for
- High pressure and temperature explosive decomposition kinetics, metal oxidation kinetics, fluid phase chemical kinetics (particularly for expanded states), carbon kinetics
- Low gas detonations (e.g. thermites)
- Liquids condensation (e.g. water, ammonia) for low (P, T) safety studies

Results (since last review)

- Materials EOS Advances -

1. **$MgCl_2$ –** Finalized determination of the 300K P-V EOS up to 30 GPa; manuscript prepared for publication; results embedded into the Cheetah thermochemical code

2. **$(C_2H_5)_3PO_4$, (TEP) –** UTDI measurements completed up to 18 GPa; unreacted Hugoniot results used to develop a TEP CHEETAH EOS; results sent directly to ARA personnel; manuscript prepared for journal submission

3. **BiI_3 –** EOS developed (based on year-three PALS measurements) and embedded into the Cheetah code

Results (since last review)

4. HI_3OI_8 – Measured P-V EOS up to 30 GPa (XRPD); results used to develop a HI_3OI_8 CHEETAH EOS; results sent directly to AFRL/RWM personnel (B. Little made/provided the sample)

5. TiF_4 – Measured preliminary P-V EOS up to 9 GPa (XRPD)
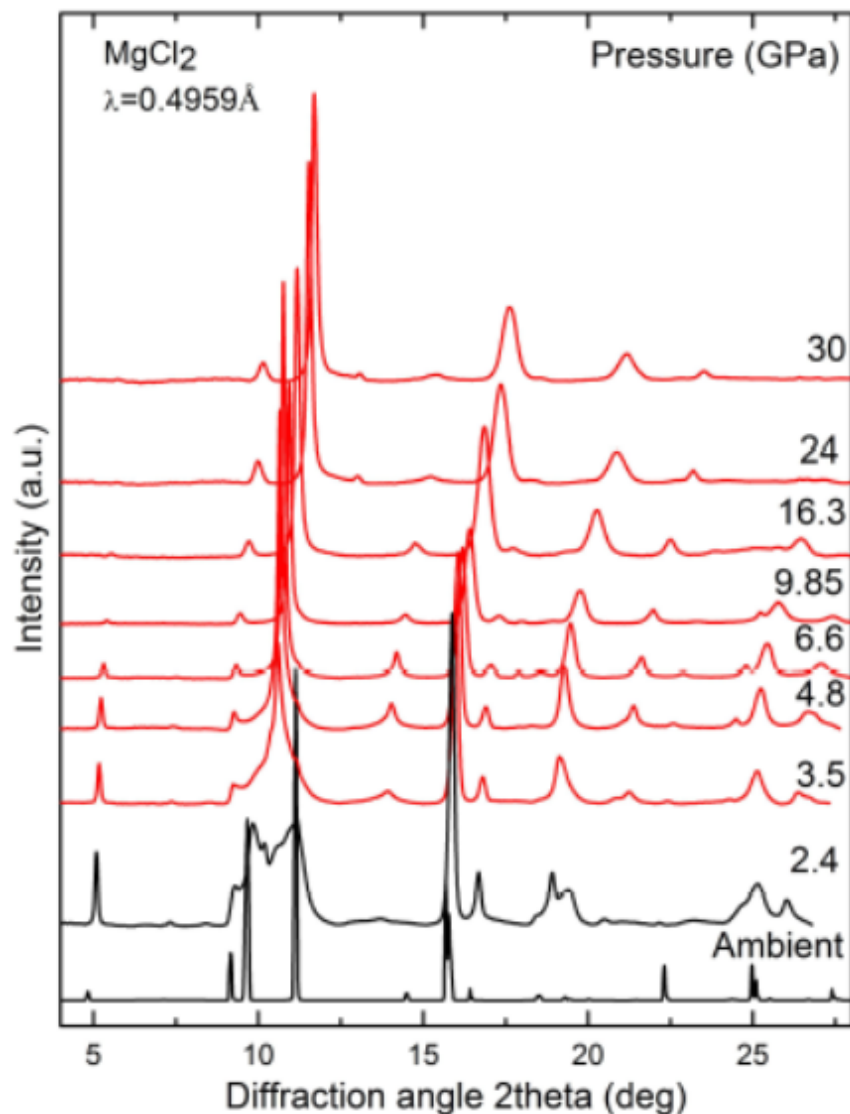
- Diagnostic Advances -

6. Jaguar laser was refurbished for sound-speed measurements

7. ICP torch developed in our lab

>enables chemical kinetics related to fire-ball induced chemistry

>TRIR and 2-photon LIF diagnostics

Published a paper on the EOSs of AlF_3 and AlI_3

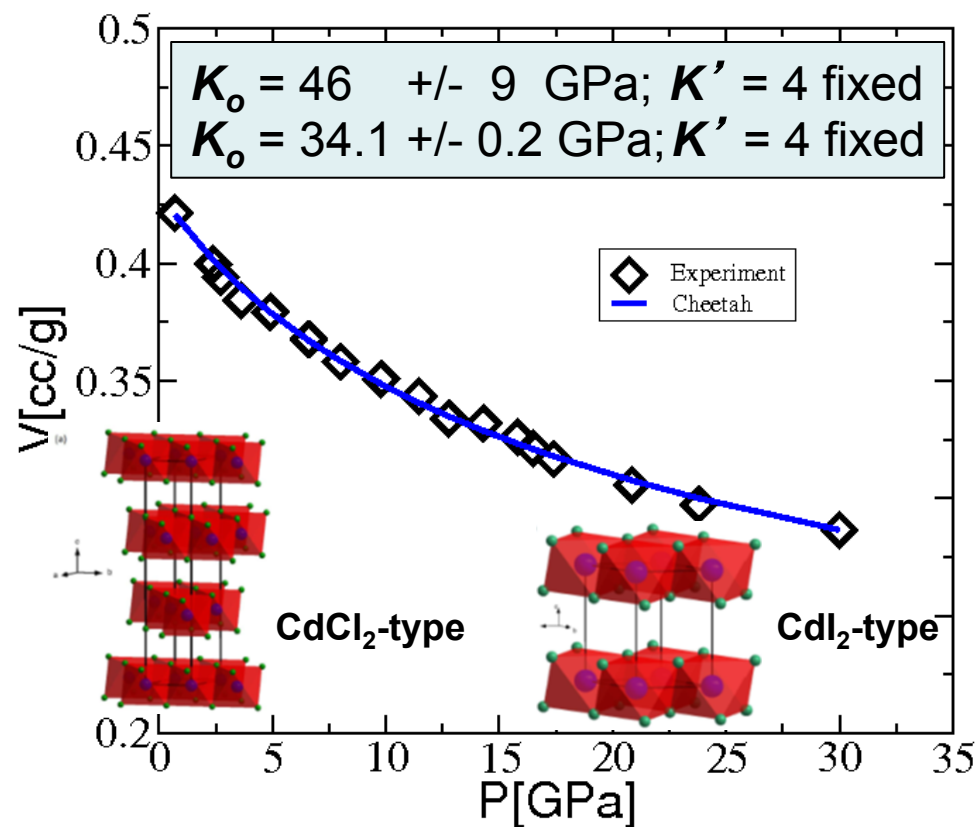E. Stavrou et al. *J. Chem. Phys.* <u>142</u>, 214506 (2015)

Results (since last review)

1. MgCl$_2$

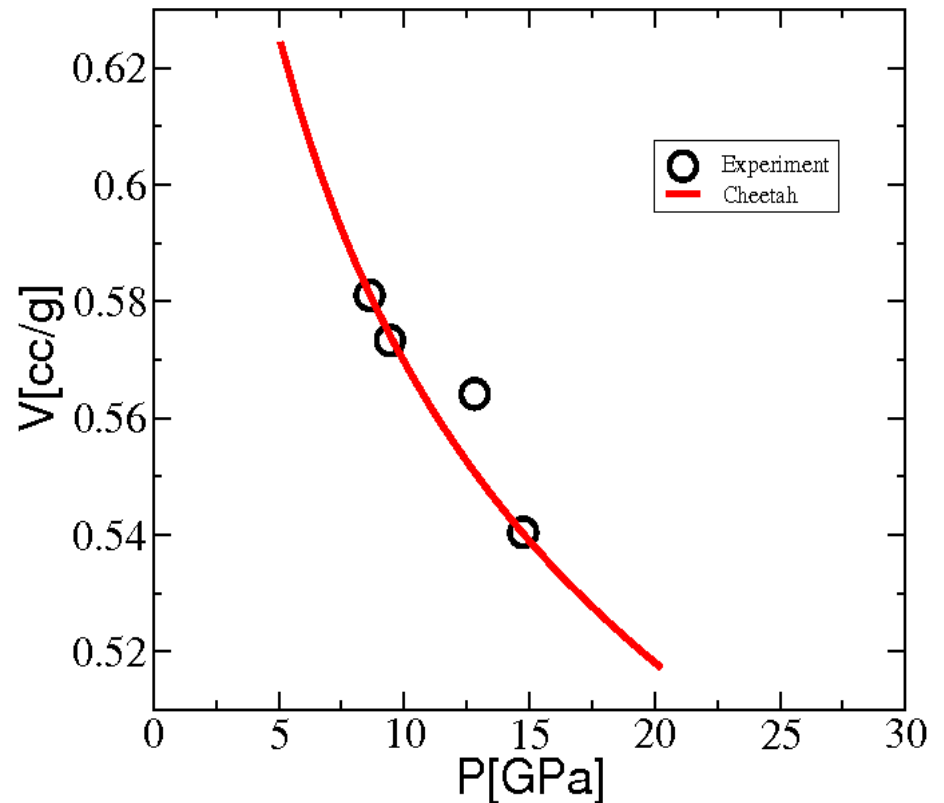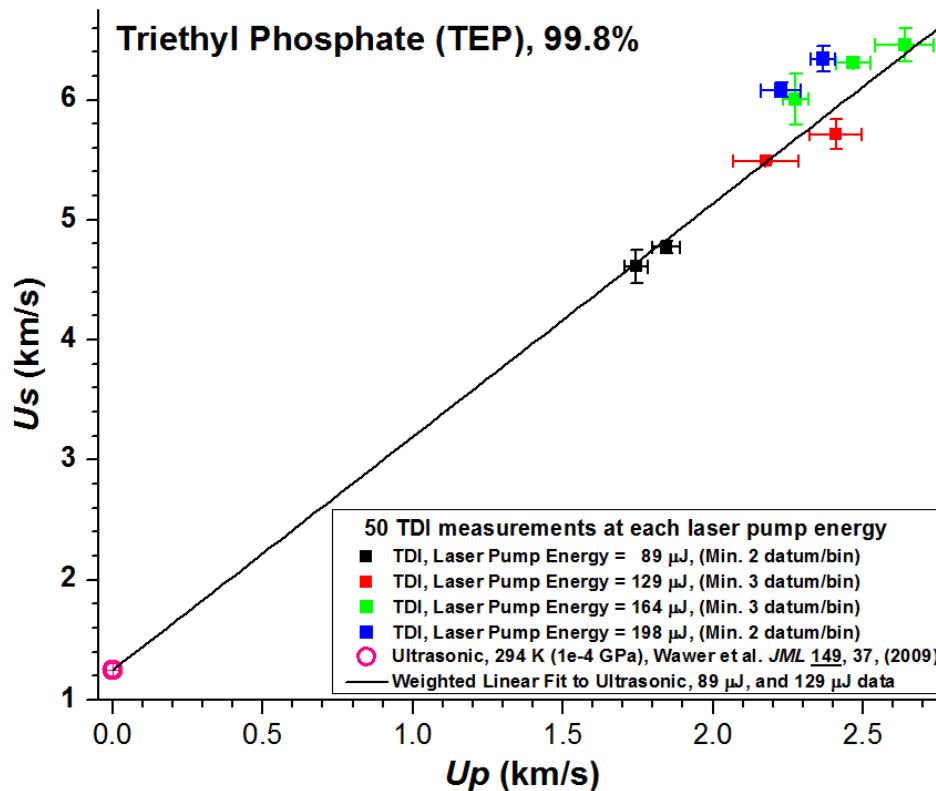2nd-order phase transition at 0.7 GPa
> rhombohedral to hexagonal

Anisotropic lattice compression
> c-axis more compressible < 10 GPa

K_o = 46   +/- 9 GPa; K' = 4 fixed
K_o = 34.1 +/- 0.2 GPa; K' = 4 fixed

CdCl$_2$-type   CdI$_2$-type
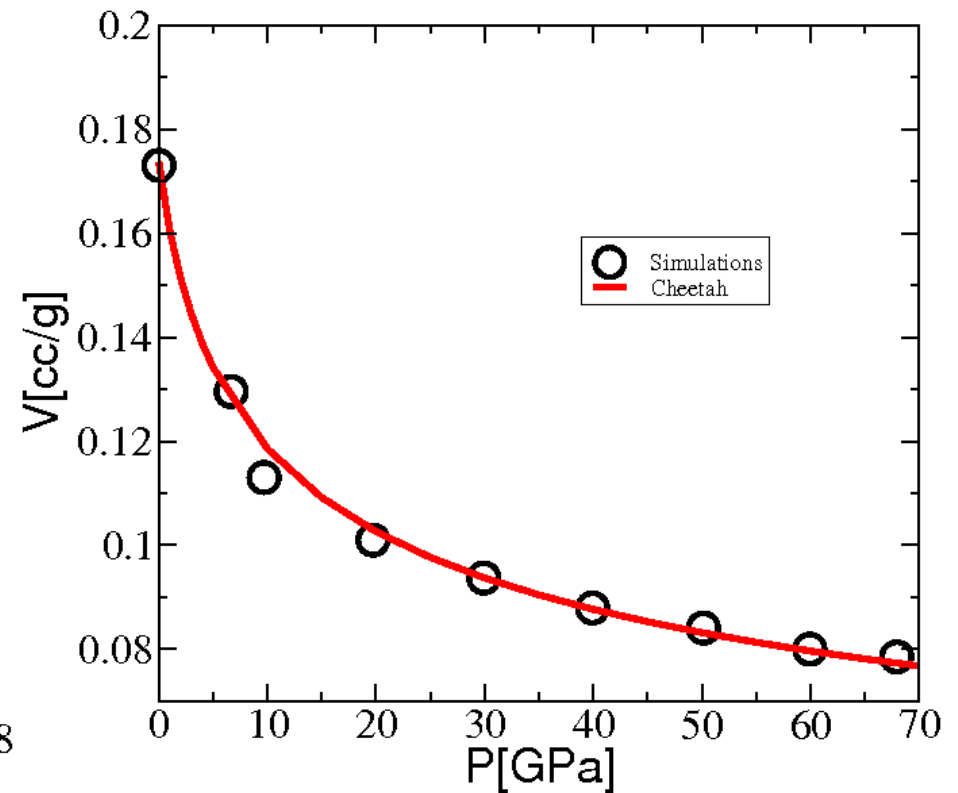
Results (since last review)

2. $(C_2H_5)_3PO_4$

200 shock data points, 50 shots per laser-drive energy

Unreacted and reacted shock Hugoniot states observed

Shock initiation threshold pressure (100 ps) is 15 GPa

Triethyl Phosphate (TEP), 99.8%

50 TDI measurements at each laser pump energy
- TDI, Laser Pump Energy = 89 μJ, (Min. 2 datum/bin)
- TDI, Laser Pump Energy = 129 μJ, (Min. 3 datum/bin)
- TDI, Laser Pump Energy = 164 μJ, (Min. 3 datum/bin)
- TDI, Laser Pump Energy = 198 μJ, (Min. 2 datum/bin)
- Ultrasonic, 294 K (1e-4 GPa), Wawer et al. *JML* 149, 37, (2009)
- Weighted Linear Fit to Ultrasonic, 89 μJ, and 129 μJ data

U_s (km/s) vs U_p (km/s)

Experiment
Cheetah

V[cc/g] vs P[GPa]
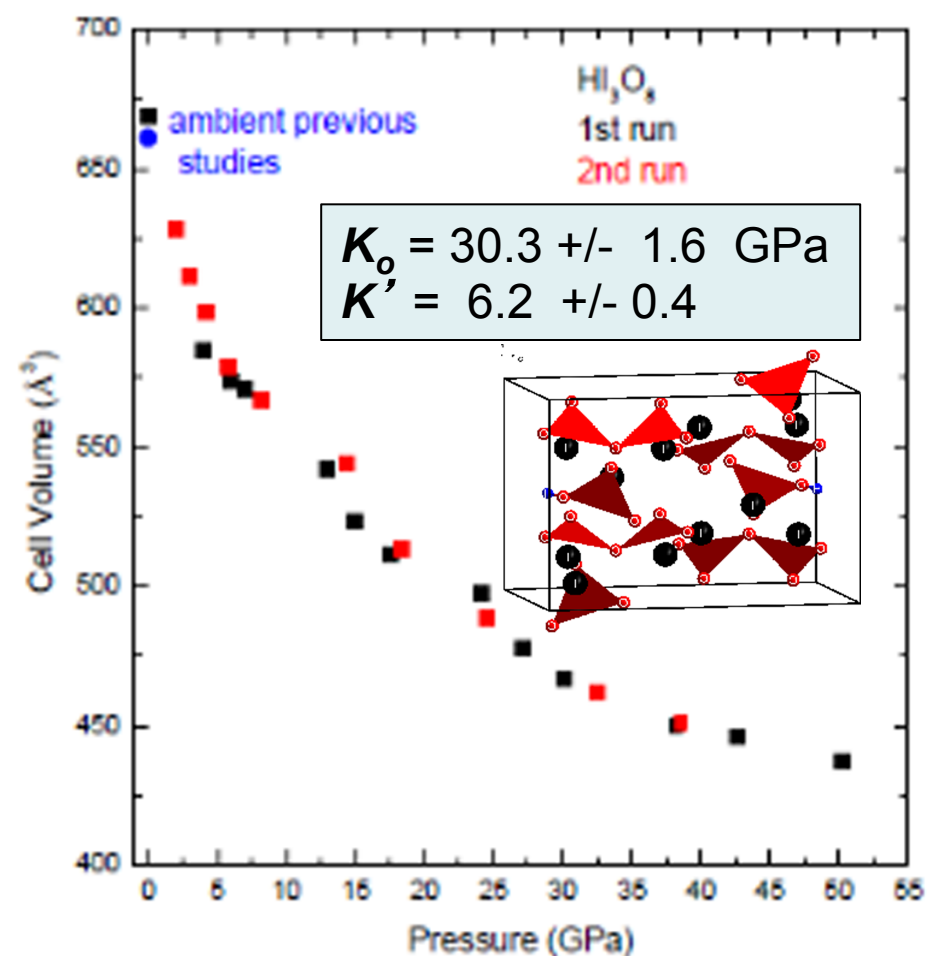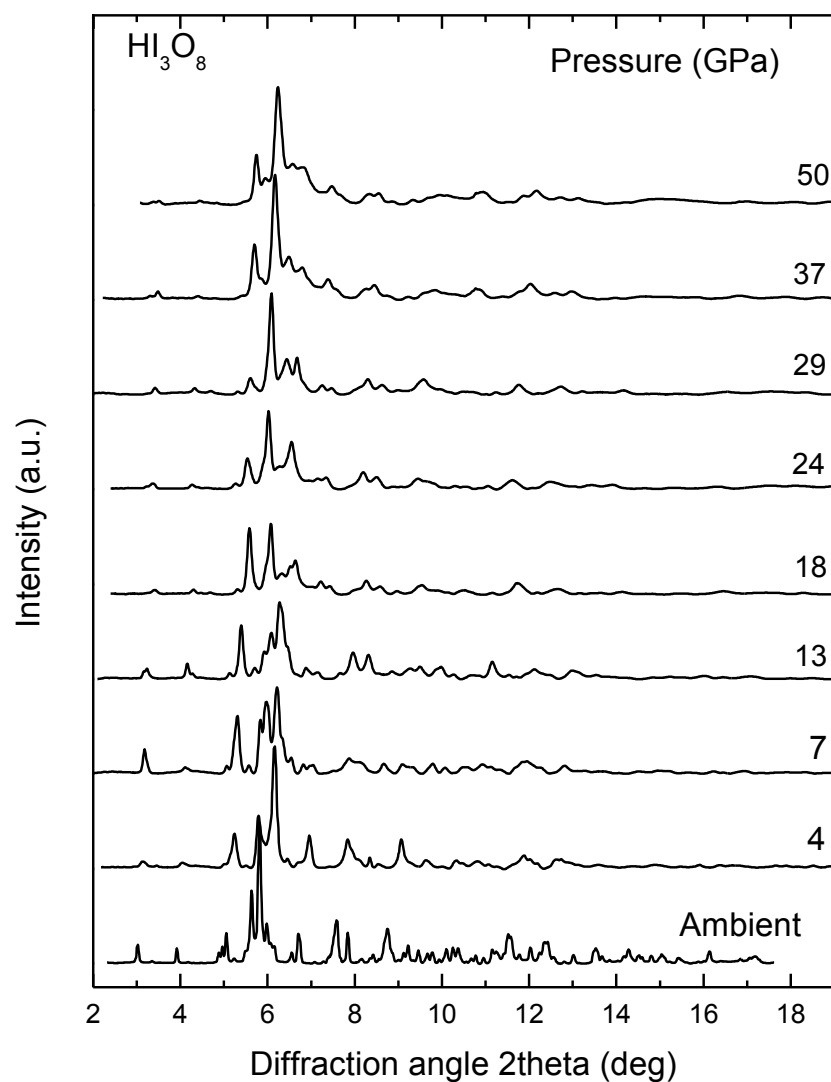
Results (since last review)

3. BiI$_3$

Semi-empirical EOS established using DFT P-V results and our year-three PALS adiabatic sound-speed measurements
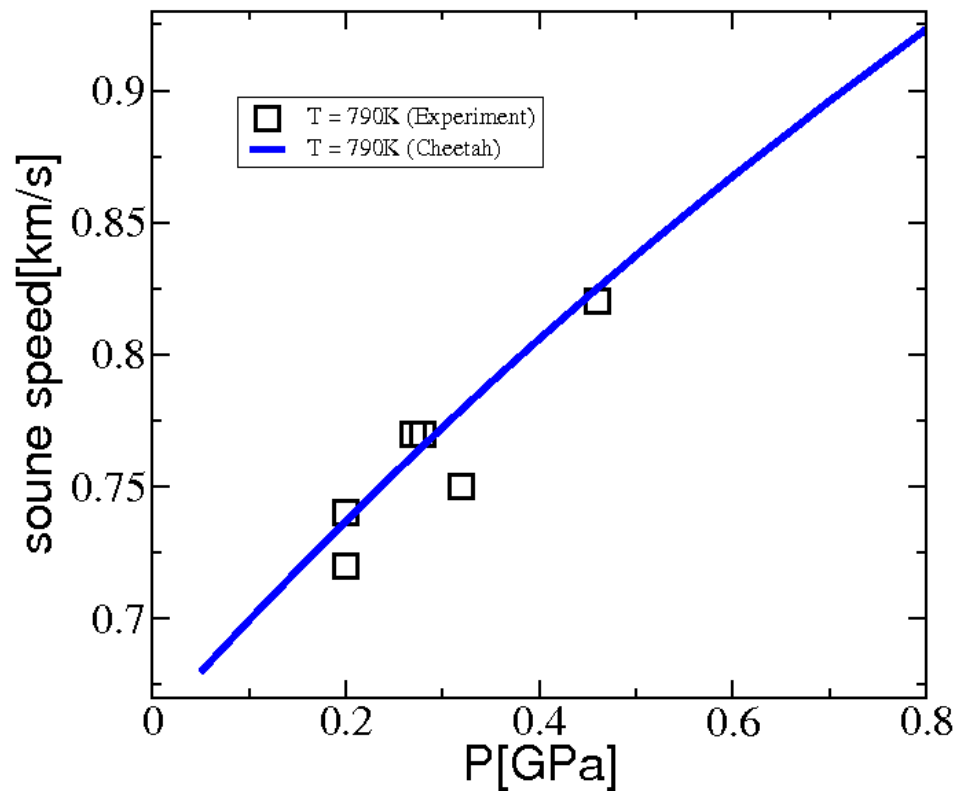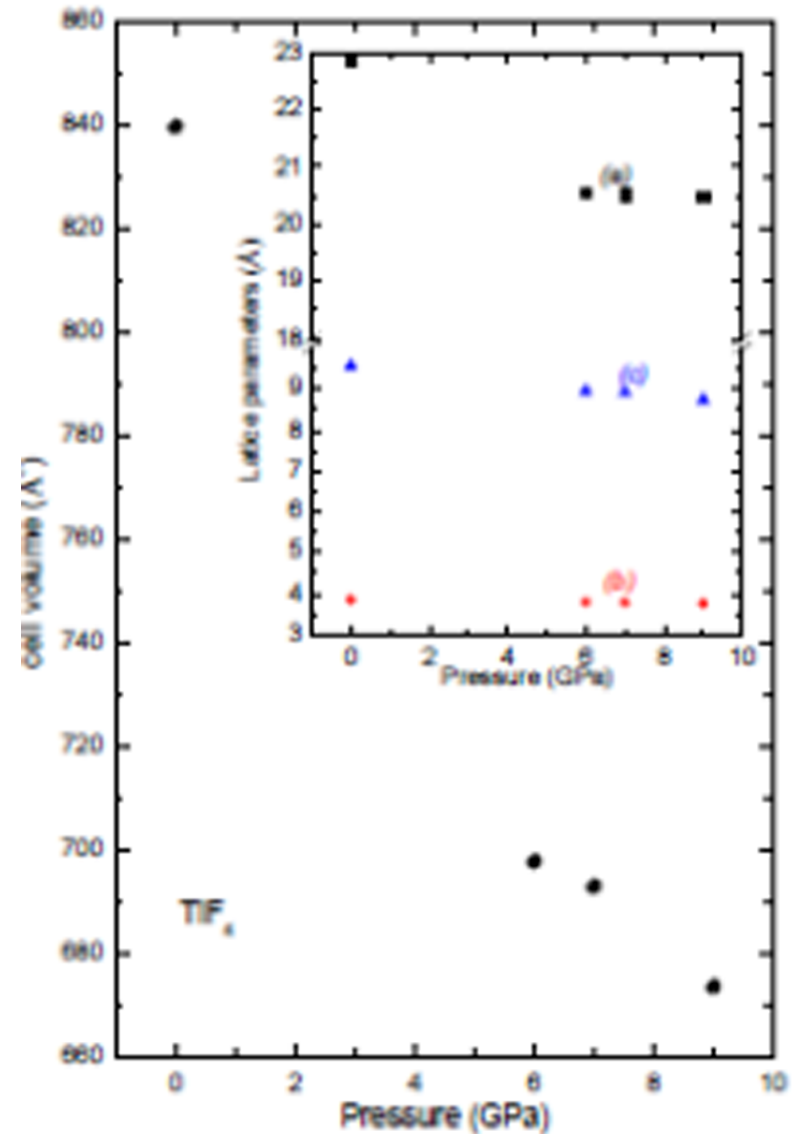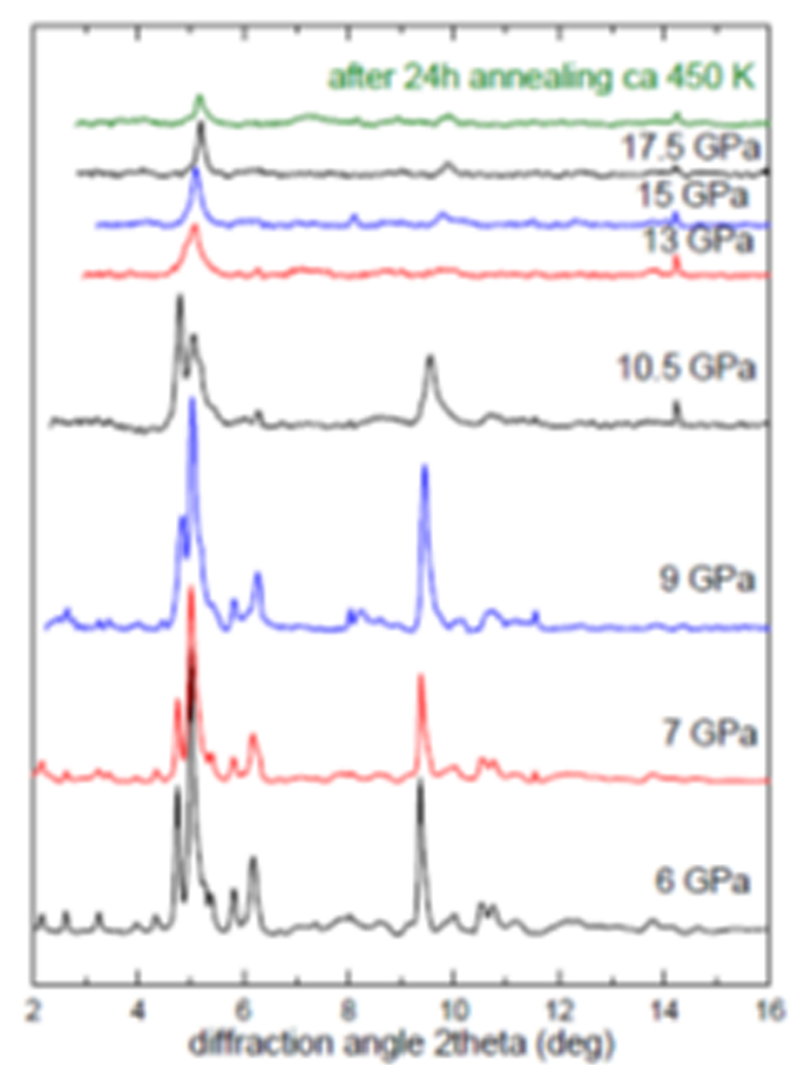
Results (since last review)

4. HI$_3$O$_8$

No structural phase transition < 50 GPa

K_o = 30.3 +/- 1.6 GPa
K' = 6.2 +/- 0.4

Results (since last review)

5. TiF$_4$

No structural phase transition < 12 GPa
Crystalline to amorphous PT at > 12 GPa

Coordination/Collaboration and Transition

- The development of a Cheetah-code Agent Defeat Toolbox (ADT) is an intensive and ongoing project

- Our template for success is the Joint Munitions Program –DOD munitions are continually optimized (user feedback and requests)

- Internal or external collaborative efforts (including Cheetah projects partially funded by other agencies) include,

  LLNL-NNSA Campaign-II High Explosives; LLNL-DHS LDRD

  DOD - Joint Munitions Program, TCGIII

  EOSs provided directly to AFRL/RWM and ARA personnel

- **>** 5-year transition - ongoing approach with DOD/DTRA users

  Continue to provide accurate semi-empirical predictions and guidance to DOD and DTRA agent defeat munition efforts

Future Directions

- Finalize TiF_4 EOS study (a JMP leveraged effort); add to Cheetah-EOS library

- Start and complete BiI_3 P-V EOS study – to test recent DFT predictions; improve/validate our existing EOS

- Start and complete BF_3 and SiF_4 sound-speed and/or P-V XRPD measurements; develop EOSs

- Submit <u>the last</u> National Lab DTRA/BAA sponsored project report; 13 EOSs; new thermochem. predictions

Continue to assist DTRA and provide HE agent defeat performance predictions in support of DTRA sponsored R&D and national defense initiatives